(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 516 248 A2**

(12) EUROPEAN PATENT APPLICATION

(21) Application number: **92202490.6**

(22) Date of filing: **02.05.89**

(51) Int. Cl.5: **C23C 28/00**, C23C 30/00, C23C 14/06, C23C 14/12

This application was filed on 12 - 08 - 1992 as a divisional application to the application mentioned under INID code 60.

(30) Priority: **02.05.88 JP 109479/88**
02.05.88 JP 109480/88

(43) Date of publication of application:
02.12.92 Bulletin 92/49

(60) Publication number of the earlier application in accordance with Art.76 EPC: **0 341 010**

(84) Designated Contracting States:
CH DE FR GB IT LI

(71) Applicant: **ORIENT WATCH CO., LTD.**
4-4, Sotokanda 2-chome Chiyoda-ku
Tokyo(JP)
Applicant: **Murayama, Youichi**
304, Domusu Mejiro, 17-44 Shimoochiai
3-chome
Shinjyuku-ku, Tokyo(JP)

(72) Inventor: **Murayama, Youichi**
304, Domusu Mejiro, 17-44, Shimoochiai
3-Chome
Shinjyuku-Ku, Tokyo(JP)

(74) Representative: **Calamita, Roberto**
Frank B. Dehn & Co., Imperial House, 15-19
Kingsway
London WC2B 6UZ(GB)

(54) Composite film.

(57) The present invention relates to a composite film comprising a metal, an alloy and/or an inorganic substance with an organic substance, which is excellent in decorative property, protection and functionality.

Methods applicable for forming such a composite film include a technique of evaporating a metal, an alloy, and/or an inorganic substance and an organic substance, simultaneously exciting the evaporated particles, and causing vapour-deposition in the state of ionized particles, neutral particles or radicals, and a method of sputtering, without excitation, etc.

The film of the present invention has excellent colour tone and wear resistance, and a frictional coefficient lower than that of a film formed from a metal, alloy or inorganic substance alone. Reduction in the consumption of expensive metals, alloys or inorganic substances is also achieved.

EP 0 516 248 A2

The present invention relates to a composite film. More particularly, the present invention relates to a composite film comprising a metal, an alloy and/or an inorganic substance with an organic substance. The film has excellent decorative, protective and functional properties.

A widely utilized procedure is the formation of a vapour-deposited thin film of a metal, an inorganic material or an organic polymer on the surface of a substrate comprising a metal, glass, ceramic material or plastics material, the thus-formed thin film being use as an insulating film, a reflecting film, an optical thin film, a display element or an electronic device. Known processes for depositing such a thin film on a substrate include vacuum vapour deposition, sputtering, ion plating, CVD, MOCVD, MBE, etc.

However, there are problems with these conventional methods. There are problems in preparing thin films having the desired properties and functions, and therefore the uses of thin films are at present limited.

One problem is that a conventional film which is excellent in colour tone, corrosion resistance, adhesion, wear resistance and other functional properties, and which is applicable as a useful surface material for watches and accessories has not as yet been achieved. Furthermore, in order to form such a film using a conventional method, it is necessary to prepare a layer comprising an expensive metal or an alloy thereof, thus resulting in difficulty in preparing a composite film excellent in decorative property, protection and functionality and which may be manufactured at a low cost.

The present invention proposes means to solve these problems by forming a composite film composed of a composite compound film, a composite multilayered film or a composite compound multilayered film, comprising a metal, an alloy and/or an inorganic substance with an organic substance. That is to say, in one aspect the present invention provides a composite film characterized in that it is formed by depositing on a substrate a metal, an alloy and/or an inorganic substance with an organic substance by simultaneous vapour-phase co-deposition. In another aspect the present invention provides a composite multilayered film formed by vapour-depositing a thin film comprising a metal, an alloy and/or an inorganic substance and an organic polymer by plasma exciting vapour phase deposition.

As the metal or the alloy in the composite compound film of the present invention, gold and/or at least one metal selected from Cu, Al, Ni, Ag, Zn, Sn, Ta, V, Cr, Co, Pt, Pd, Ru, Rh, Ti, W, Mo, Ir, Cd, Sb, Hf, Ga, Si, Fe, Y, Ba, Ge, Zr, Nb and In or an alloy thereof may be used. As the inorganic substance, TiN, TaN, ZrN, TaC, VN and/or C may be employed.

Applicable organic substances include polycarbonate, polyacrylate, polysiloxane, polyester, polyolefin, and polyethylene.

Depending upon the material of the substrate on which the composite film is to be formed, an undercoat comprising a metal, an alloy, an inorganic substance and/or an organic substance may be formed on the surface of the substrate, and further a composite compound film may be stacked thereon integrally therewith.

It is also possible to arrange a composite compound film as described above on the surface of a substrate, and stack an outer coat comprising a metal, an alloy, an inorganic substance and/or an organic substance thereon integrally therewith.

Furthermore, it is possible to form an undercoat comprising a metal, an alloy, an inorganic substance and/or an organic substance on the surface of a substrate, stack a composite compound film thereon, and form an outer coat comprising a metal, an alloy, an inorganic substance and/or an organic substance thereon integrally therewith.

Methods applicable for forming such a composite compound film include a technique of evaporating a metal, an alloy, and/or an inorganic substance an an organic substance, simultaneously exciting the evaporated particles, and causing vapour-deposition in the state of ionized particles, neutral particles or radicals, and a method of sputtering, without excitation, etc. In terms of colour tone and adhesion strength, it is desirable to integrally form the film in the excited state.

In this case, evaporated particles should preferably be excited in a vacuum reactor by glow discharge and be plasma-ionized particles. The methods applicable for plasma-ionization include ion-plating processes such as the hollow cathode method and high-frequency excitation, and plasma CVD. For an organic substance, it is also possible to sue the method of polymer evaporation or introduction of monomer gas and vapour-depositing it through plasma polymerization.

For excitation, light radiation such as a laser beam may be applied. In using the ion-plating method, an inert gas such as argon may be introduced into a vacuum reactor, for example, maintained in a vacuum at a pressure of from 10^{-2} to 10^{-5} Torr. The temperature of the substrate may be within the range of from room temperature to about 400°C. A reactive gas such as oxygen, nitrogen, ammonia, hydrogen carbide, hydrogen sulfide, or hydrogen fluoride may be introduced for vapour deposition by reactive ion-plating. In this case, the gas pressure should preferably be at least 10^{-4} Torr.

By the present invention, as described above, it is possible to achieve a composite compound

film excellent in colour tone, having a satisfactory adhesion strength and having such functional properties as dielectric property, conductivity and light response.

In the present invention, the composite compound multilayered film may, for example, be formed by vapour-depositing an organic polymer film on the surface of a substrate comprising a metal, an alloy, ceramics or plastics, and then sequentially forming a thin film comprising a metal, an alloy and/or an inorganic substance, and an organic polymer layer, or formed by vapour-phase depositing a thin film comprising a metal, an alloy and/or an inorganic substance, then an organic polymer film, and subsequently, a thin film comprising a metal, an alloy and/or an inorganic substance.

The thin film comprising a metal, an alloy and/or an inorganic substance in the present invention may, for example, be gold, a gold alloy or TiN, and not limited to these examples, a metal, an alloy or an inorganic substance having the desired colour tone and gloss. Examples of the metal or the alloy used in the present invention include such elements as gold, Cu, Al, Ni, Ag, Zn, Sn, Ta, V, Cr, Co, Pt, Pd, Ru, Rh, Ti, W, Mo, Ir, Cd, Sb, Hf, Ga, Si, Fe, Y, Ba, Ge, Zr, Nb and In or an inorganic substance comprising a compound thereof such as TiN, TaN, ZrN, TaC, VN and/or C.

The organic polymer may be present as a separate film which may be a thin film comprising a polymer such as polycarbonate, polyacrylate, polysiloxane, polyester, polyolefin, or polyethylene. In this case, a dye compound or a pigment could be vapour-deposited for colouring.

There is no particular limitation for the substrate, which may be a glass, a metal, an alloy, a ceramic material or a plastics material.

The thin film comprising a metal, an alloy and/or an inorganic substance and the organic polymer film as listed above may be formed by plasma-exciting particles produced through evaporation of the material and vapour-depositing the resultant ionized particles, neutral particles or radicals. It is also possible to form a thin film of metal or alloy, not by excitation, but by sputtering, etc. However, with a view to largley improving the colour tone, adhesion strength and wear resistance of the composite multilayered film, it is desirable to integrally form it by plasma excitation.

The evaporated particles should preferably be excited by glow discharge in a vacuum reactor for plasma ionization. Means for plasma ionization convenient in this case include ion plating such as the hollow cathode method and the high-frequency excitation method, and plasma CVD. When forming the organic polymer film, plasma excitation may be applied by evaporating the polymer or introducing a monomer gas for vapour deposition. Laser beam excitation may also be applied.

When applying the ion plating method, an inert gas such as argon could be introduced into a vacuum reactor kept in vacuum at a pressure of, for example, from 10^{-2} to 10^{-5} Torr. The substrate temperature may be within the range of from room temperature to about 400°C. When forming an inorganic thin film, vapour deposition could be preferably carried out by ion plating through introduction of a reactive gas such as oxygen, nitrogen, ammonia, hydrogen carbide, hydrogen sulfide, or hydrogen fluoride. In this case, the gas pressure should preferably be at least 10^{-4} Torr.

By the present invention, as described above, it is possible to achieve a low-cost composite film excellent in colour tone, having a satisfactory adhesion strength, and having such functional properties as dielectric property, conductivity and light response.

The present invention will now be illustrated by means of the following non-limiting Examples.

In the following examples reference will be made to the accompanying drawings in which:

Fig. 1 is a partial sectional view illustrating an embodiment of the composite compound film of the present invention, in which a gold composite compound film is vapour-deposited on a substrate having a previously deposited TiN layer;

Fig. 2 is a partial sectional view illustrating an embodiment of the present invention, in which an undercoat is made on TiN layer deposited on a substrate, and a gold composite compound film is formed on the undercoat;

Fig. 3 is a partial sectional view illustrating an embodiment of the present invention, in which a gold composite compound film is formed on a TiN layer stacked on a substrate, and an outer coat is vapour-deposited thereon;

Fig. 4 is a partial sectional view illustrating an embodiment where an undercoat is made on a TiN layer deposited on a substrate, a gold composite compound film being formed thereon, and a top coat is vapour-deposited further thereon;

Fig. 5 is a partial sectional view illustrating an embodiment where a transparent conductive film is formed on the surface of the composite compound multilayered film shown in Fig. 3;

Fig. 6 is a partial sectional view illustrating a case where a composite compound film is formed on the composite compound multilayered film shown in Fig. 3, and

Figs. 7 and 8 are sectional views illustrating typical composite films of the present invention.

Example 1·

A composite film was formed using an ion plating apparatus based on the high-frequency excitation method. Figure 1 illustrates this example. A stainless steel sheet was used as the substrate (1). The stainless steel sheet was bombarded by introducing argon gas under a pressure of 5 x 10^{-3} Torr, and then a TiN thin film (2) was vapour-deposited by reactive ion plating with nitrogen gas and evaporated Ti particles under a pressure of 8 x 10^{-4} Torr. A TiN thin film (2) having a thickness of 0.2 micrometres was formed by reaction for three minutes under conditions including a discharge power of 300 W and a substate temperature of 100 °C.

Then, under an argon pressure of 4 x 10^{-3} Torr, evaporated particles of gold and polycarbonate were plasma-ionized to form a composite compound film (3) on the surface of the TiN thin film (2) on the substrate (1). As a result, a composite compound film (3) having a colour tone equal to that of gold was obtained, with a wear resistance about twice as high as that available in vapour deposition of gold on the substrate. As to adhesion strength, no peel off was observed in a bend test of 90°, and an excellent corrosion resistance was shown.

Example 2

In a manner similar to that in Example 1, a substrate (1) having a titanium nitride thin film (2) formed thereon was used, as shown in Fig. 2, and under an argon pressure of 4 x 10^{-3} Torr, evaporated polycarbonate particles were plasma-ionized on to the titanium nitride thin film. Thus, an undercoat (4) (with regard to the ultimate outer layer) was formed by vapour-depositing a polymer film (polycarbonate) on the substrate.

Subsequently, gold-chromium alloy (with a chromium content of 2%) was evaporated together with polycarbonate to form a composite compound film (3) of polycarbonate and gold chromium alloy with a thickness of about 0.2 micrometres on the polycarbonate polymerization film.

The thus-formed film has a colour tone identical with that of gold-chromium alloy, with such an excellent adhesion that no separation was observed in a 90° bend test, as well as high wear resistance and corrosion resistance.

Example 3

As shown in Fig. 3, a polycarbonate polymer film was vapour-deposited as the top coat (5) under an argon pressure of 4 x 10^{-3} Torr on the surface of the composite compound film (3) obtained in Example 1. As a result, a hard transparent polymer film was obtained. This composite compound multilayered film had a colour tone identical with that of gold, with a gloss, and showed an elegant appearance. This transparent polymer film was excellent in protection of the composite film, as well as in adhesion, wear resistance and corrosion resistance as in Example 1.

Example 4

As in Example 1, a substrate (1) having a titanium nitride thin film (2) formed thereon was used as shown in Fig. 4 and under an argon pressure of 4 x 10^{-3} Torr, evaporated polycarbonate particles were plasma-ionized. Thus, a polymer film was vapour-deposited as the undercoat (4) on the substrate.

Then, gold chromium alloy (with a chromium content of 2%) was evaporated together with polycarbonate to form a composite compound film (3) of polycarbonate and gold-chromium alloy having a thickness of about 0.2 micrometres on the polycarbonate polymer film.

Subseqently, evaporation of gold-chromium alloy was discontinued, and a polymer film comprising polycarbonate alone having a thickness of about 0.2 micrometre was formed as the top coat (5) by vapour deposition on the composite film.

The thus-formed film had colour tone identical with that of gold-chromium alloy, with such an excellent adhesion that no separation was observed in a 90° bend test, as well as high wear resistance and corrosion resistance.

Example 5

As shown in Fig. 5, a 0.3 micrometre-thick ITO (transparent conductive substance) film (6) was formed on the surface of the composite multilayered film obtained in Example 3, with ITO as the evaporation source under conditions including an oxygen gas pressure of 3 x 10^{-4} Torr, a discharge power of 300 W and a substrate temperature including the composite compound film (3) of Example 4 of 200 °C. The thus-obtained composite compound multilayered film had a colour tone of gold and a gloss, resulting in an elegant appearance. Protection provided by the composite film was further improved, with excellent adhesion, wear resistance and corrosion resistance as in Example 1, and had a surface conductivity (resistance: 200Ω/□)

Example 6

A composite multilayered film was formed by an ion plating apparatus based on high-frequency excitation. As shown in Fig. 7, a stainless steel sheet was used as the substrate (11).

The stainless steel sheet was bombarded by introducing argon gas under conditions of up to a pressure of 5×10^{-5} Torr, and then, a TiN thin film (12) was vapour-deposited by reactive ion plating with nitrogen gas and evaporated Ti particles under a pressure of 8×10^{-4} Torr. A 0.2 micrometre-thick TiN thin film (12) was formed through reaction for three minutes under conditions including a discharge power of 300 W and a substrate temperature of 100 °C.

A polymer film (13) was vapour-deposited by plasma-ionizing evaporated particles of polycarbonate under an argon pressure of 4×10^{-3} Torr. Then, a gold thin film (14) was formed through plasma-ionization of evaporated gold particles under an argon pressure of 3×10^{-3} Torr.

This resulted in a multilayered film excellent in gold colour tone. All properties such as colour tone, adhesion strength and wear resistance were far superior to those available in the absence of an organic polymer film, and wear resistance was about twice as high.

Example 7

A polycarbonate polymer film was vapour-deposited under an argon pressure of 4×10^{-3} Torr on the surface of the composite multilayered film obtained in Example 6. A hard transparent polymer film was obtained, with a glossy gold colour tone giving an elegant appearance. The film had excellent surface protective properties.

Example 8

A transparent polyacrylate polymer layer and a thin gold film were vapour-deposited on a glass substrate as in Example 6. The gold film showed a satisfactory colour tone and wear resistance was about twice as high as that available without vapour deposition of the polyacrylate polymer film.

Example 9

Polycarbonate polymer film (17) and an ITO (transparent conductive substance) film (18) were sequentially vapour-deposited on the surface of the multilayered film comprising a polyacrylate polymer film (15) and a thin gold film (16) obtained in Example 6, as shown in Fig. 8. The resultant composite multilayered film had a colour tone of gold and a satisfactory surface conductivity (resistance: 200Ω/□).

The ITO thin film was formed, with ITO as the evaporation source, under conditions including an oxygen pressure of 3×10^{-4} Torr, a discharge power of 300 W, and a substrate temperature of 30 °C. It is a 0.3 micrometre-thick transparent conductive film.

Example 10

A composite compound film was formed using a high frequency sputtering apparatus. A stainless steel sheet was used as the substrate. After presputtering for about 15 minutes by introducing argon gas under a pressure of 5×10^{-3} Torr, nitrogen gas was introduced under a pressure of 5×10^{-4} Torr using TiN as the target. Then, argon was introduced up to a pressure of 2×10^{-2} Torr, and sputtering was conducted for two hours by applying a high-frequency power of 10 W/cm^2 to form a TiN film having a thickness of about 0.5 micrometre. Subsequently, the target was replaced with Au (containing 1% Cr), and sputtering was conducted for about 10 minutes with a high-frequency power of 2 W/cm^2 by introducing ethylene (C_2H_4) up to 1×10^{-4} Torr and adding argon gas up to 5×10^{-3} Torr. A composite compound film comprising gold-chromium alloy and ethylene was thus obtained, having a gold colour tone, and being excellent both in adhesion and corrosion resistance.

Example 11

A composite compound multilayered film was formed using a high-frequency ion plating apparatus. A nickel-plated brass sheet was used as the substrate. After introducing argon gas up to 5×10^{-4} Torr, ion bombardment was conducted at a high-frequency power of 500 W and a DC electric field of -200V for about 15 minutes. Then, titanium was evaporated using an electron gun, by introducing argon gas up to 8×10^{-4} Torr, under discharge conditions including a high-frequency power of 500W, and a DC electric field of -200V, to form a TiN film having a thickness of about 1 micrometre in 30 minutes. Subsequently, the substrate was transferred to a high frequency sputtering apparatus, in which sputtering was conducted for about 10 minutes, with Au (containing 1% Cr) as the target, by introducing ethylene (C_2H_4) up to 1×10^{-4} Torr and adding argon gas up to 5×10^{-3} Torr with a high-frequency power of 2W/cm^2 to obtain a composite compound film comprising gold-chromium alloy and ethylene. The resultant film had a gold colour tone and was excellent both in adhesion and in corrosion resistance.

Example 12

A composite compound film was formed using a high-frequency sputtering apparatus. A nickel-plated brass sheet was used as the substrate. After sputtering for about 15 minutes by introducing argon gas up to 5×10^{-3} Torr, nitrogen gas at 5 x

10^{-4} Torr was introduced, with a TiN target, and then, sputtering was carried out for two hours with a high-frequency power of 10W/cm² by introducing argon up to 2×10^{-2} Torr to form a TiN film having a thickness of about 0.5 micrometre. Subsequently, the substrate was transferred to an ion plating apparatus, in which gold (containing 1% Cr) was evaporated in a resistance-heating type boat under discharge with a high-frequency power of 40 W by introducing ethylene gas to 4×10^{-4} Torr, and a composite film comprising gold-chromium alloy and ethylene having a thickness of about 1 micrometre was formed in 10 minutes. The formed film was excellent in adhesion, wear resistance and corrosion resistance.

Example 13

A composite compound film was formed by a high-frequency ion plating-apparatus. A glass plate (Corning 7059) was used as the substrate. After ion bombardment conducted for 15 minutes under conditions including a high-frequency power of 300 W and a DC electric field of -200V by introducing argon gas up to 5×10^{-4} Torr, butadiene gas was introduced up to 5×10^{-4} Torr, and a 1,000Å composite compound film was formed in about 10 minutes by evaporating germanium in a resistance-heating type boat under discharge of high-frequency power of 50 W. This film showed negative resistance-temperature characteristics and a specific resistance of from 10^{-4} to 10^{-5} Ωcm.

Example 14

A composite compound film was formed using a high-frequency ion plating apparatus. A glass plate (Corning 7059) was used as the substrate. After ion bombardment conducted for 15 minutes under conditions including a high-frequency power of 300W and a DC electric field of -200V by introducing argon gas up to 5×10^{-4} Torr, ethylene gas was introduced up to 5×10^{-4} Torr, and a 2,000Å composite compound film was formed in about 10 minutes by evaporating In (Indium) in a resistance-heating type heat under discharge of a high-frequency power of 50 W. This film was transparent and showed negative resistance-temperature characteristics.

Example 15

A composite compound film was formed using a high-frequency ion plating apparatus. An aluminium plate was used as the substrate. After ion bombardment conducted for 15 minutes under conditions including a high-frequency power of 300 W and a DC electric field of -200 V by introducing argon gas up to 5×10^{-4} Torr, ethylene gas was introduced up to 5×10^{-4} Torr, and a 200 Å composite compound film of Ni-Cr alloy and ethylene was formed in about 10 minutes by evaporating an Ni-Cr alloy in a resistance-heating type boat under discharge of a high-frequency power of 50 W. This film had a temperature coefficient of about ± 10 ppm/degC, and a high specific resistance of 500 μΩcm, thus permitting use as a high resistance element.

As described above in detail, the present invention provides the following industrially useful effects by comprising forming a composite film on a substrate through vapour-phase deposition of a metal, an alloy and/or an inorganic substance and an organic substance, and simultaneously using as required a top coat, an undercoat, or a top coat and an undercoat;

1. It is possible to reduce the consumption of the metal, alloy or inorganic substance without changing the colour tone of the metal, the alloy or the inorganic substance used.
2. The composite compound film having an organic substance can have a frictional coefficient lower than that of a film formed from a metal, an alloy or an inorganic substance alone, and wear resistance can be improved over that of a film comprising only the material of the composite film.
3. In a film formed from a metal, an alloy or an inorganic substance alone, corrosion resistance may be affected by the occurrence of pinholes. In the composite compound film, in contrast, corrosion resistance can be largely improved.
4. The composite film as applied to an article in direct touch with human skin gives a lower sensation of coldness than when human skin touches a metal, an alloy or an inorganic substance. Moreover the composite film can prevent allergy to Ni ions, etc.
5. It is possible to provide the surface a composite film with conductivity, so that conductive films of various colour tones can be prepared.

These merits are particularly effective when applying the present invention to an accessory, a watch, glasses and other articles of utility, thus providing a very wide range of applications including display elements using various colour tones as part of the design thereof.

Claims

1. A composite multilayered film comprising a thin film comprising a metal, an alloy, and/or an inorganic substance, and an organic polymer film formed by vapour phase plasma exciting deposition on a substrate.

2. A composite multilayered film as claimed in claim 1, wherein said film has a layer comprising gold or its alloy, and an inorganic substance selected from TiN, TaN, ZrN, VN, TaC and/or C.

3. A composite multilayered film as claimed in claim 1, wherein said film has a layer comprising gold and/or at least one metal selected from Cu, Al, Ni, Ag, Zn, Sn, Ta, V, Cr, Co, Pt, Pd, Ru, Rh, Ti, W, Mo, Ir, Cd, Sb, Hf, Ga, Si, Fe, Y, Ba, Ge, Zr, Nb and In, or an alloy thereof.

4. A composite multilayered film as claimed in claim 1, wherein said film comprises a transparent polymer film comprising polycarbonate, polyacrylate, polysiloxane, polyester, polyolefin and/or polyethylene.

5. A composite multilayered film as claimed in claim 1, wherin said film includes an organic polymer layer as an intermediate layer.

FIG. 1

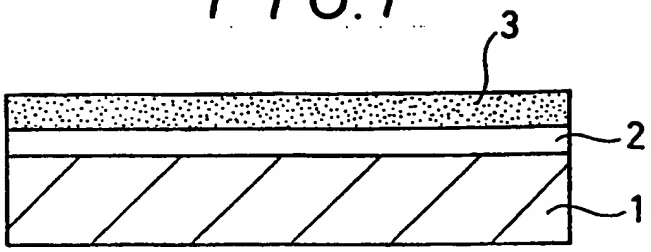

FIG. 2

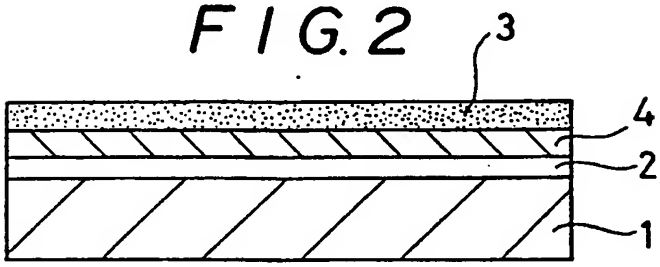

FIG. 3

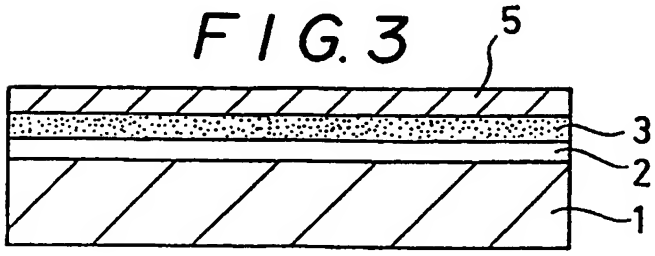

FIG. 4

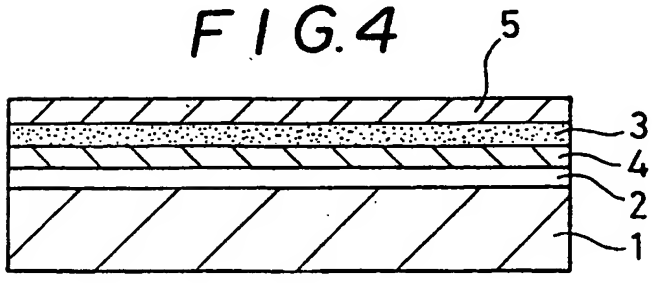

FIG. 5

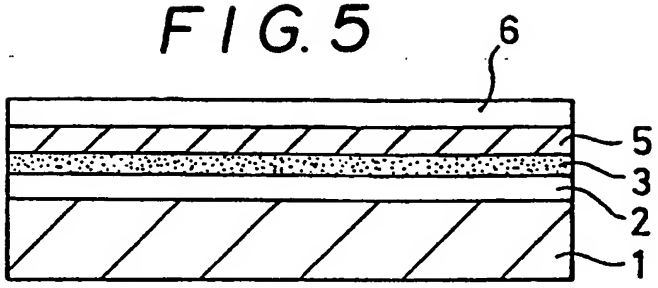

FIG. 6

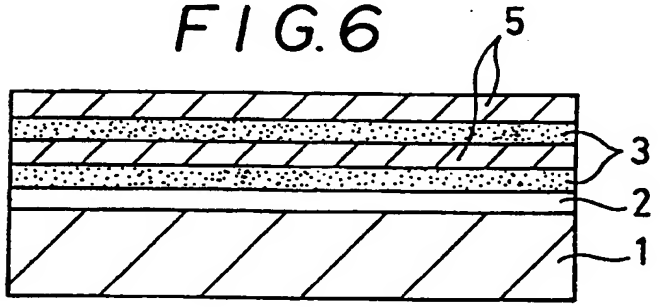

FIG. 7

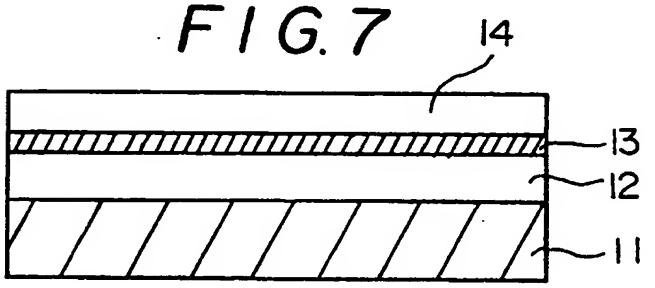

FIG. 8